Australian Government

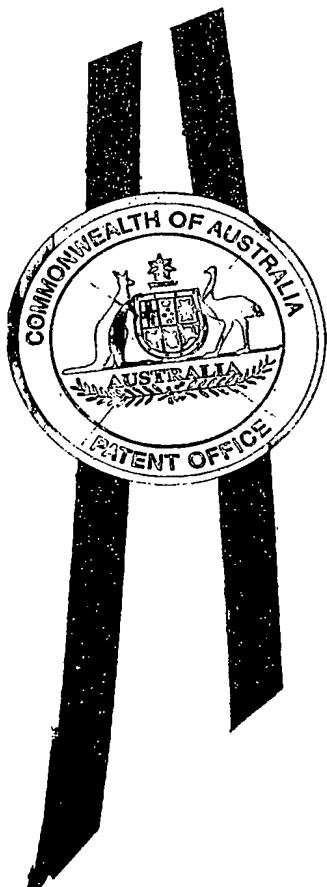**Patent Office
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I, JULIE BILLINGSLEY, TEAM LEADER EXAMINATION SUPPORT AND SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. 2003905779 for a patent by POLYMERS AUSTRALIA PTY LTD as filed on 21 October 2003.

WITNESS my hand this
Ninth day of April 2004

JULIE BILLINGSLEY .
TEAM LEADER EXAMINATION
SUPPORT AND SALES

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PROVISIONAL SPECIFICATION

Invention Title: **Fire resistant systems comprising a sacrificial layer**

The invention is described in the following statement:

FIRE RESISTANT SYSTEMS COMPRISING A SACRIFICIAL LAYER

The present invention relates to fire resistant systems involving polymer-containing compositions that form protective and/or insulating ceramic coatings when subjected to

5 high temperatures. More specifically, the present invention relates to fire resistant systems incorporating a sacrificial layer which minimises or avoids bonding between the ceramic coating and the underlying substrate it is desired to protect. The invention is particularly useful for production of fire resistant electrical cables, i.e. where the substrate is an electrical conductor.

10

There are numerous situations where it is desired to render a substrate resistant to fire. For instance, fire performance cables are required to continue to operate and provide circuit integrity when they are subjected to fire and there are many standards for cables of this type. To meet some of these standards, cables must typically maintain electrical circuit

15 integrity when heated to a specified temperature (e.g. 650, 750, 950, 1050°C) in a prescribed way for a specified time (e.g. 15 min., 30 min., 60 min., 2 hours). In some cases the cables are subjected to regular mechanical shocks during the heating stage. Often they are also subjected to a water jet or spray either in the later stages of the heating cycle or after the heating stage.

20

These requirements for fire performance cables have been met previously by wrapping the conductor of the cable with tape made with glass fibres and coated with mica. Such tapes are wrapped around the conductor during production and then at least one insulative layer is subsequently applied. Upon being exposed to increasing temperatures, the outer

25 insulative layer(s) are degraded and fall away, but the glass fibres hold the mica in place. These tapes have been found to be effective for maintaining circuit integrity in fires, but are quite expensive. Further, the process of wrapping the tape around the cable is relatively slow compared with other cable production steps, and thus wrapping the tape slows overall production of the cable, again adding to the cost. Costs could be reduced by

30 avoiding the use of tapes and extruding a cable coating consisting of a flexible polymeric

composition which turns into an insulating ceramic when exposed to fire to provide continuing circuity integrity.

Indeed, such ceramic forming compositions are well known. For instance, US 4,269,753

5   and US 4,269,757 describe coatings of this type being applied directly to a short length of copper wire. When the coated wire is exposed for 30 minutes to air at 850°C, the coatings are said to form a strong and hard ceramic substance without any cracks and without separating from the copper wire. US 6,387,518 shows application of a ceramic forming coating to an electrical conductor and the retention of circuit integrity when this is heated

10 for 2 hours at 930°C with an applied potential of 500 volts.

Problems can arise with the incorporation of these ceramic-forming compositions into cable designs where the composition is in direct contact with the metal conductor. During exposure at elevated temperature, and during subsequent cooling, the metallic conductor

15 will expand and contract at a different rate from the ceramic which is formed during the heating process. Even if the ceramic shows good shape retention during formation, this difference in thermal expansion and contraction causes the (brittle) ceramic to crack and may lead to dislodgment of part of the insulative ceramic coating, exposing the conductor and compromising circuit integrity. This cracking of the ceramic layer tends to be most

20 pronounced during the cooling stage. The problem is accentuated when the ceramic is itself strong and bonds strongly to the conductor surface (or oxide layer formed on the surface of the conductor) during the fire. For example, with copper conductors this can lead to fracture at the cuprous oxide – cupric oxide interface and dislodgment of pieces of ceramic bonded to the cupric oxide. Whilst this problem has been described with

25 particular reference to metallic conductors used in cable applications, it will be observed in any situation where a substrate coated with the type of fire resistant composition described has a different coefficient of thermal expansion from the ceramic formed when the composition is exposed to elevated temperature. The extent of the problem will depend upon the magnitude of the difference in coefficient of thermal expansion and the strength

30 of the bond formed at the interface.

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With respect to cable design, it is desirable that the residual ceramic be physically strong to resist mechanical damage and dislodgment during fire testing. However, compositional changes that increase the strength of the resulting ceramic often unacceptably increase the electrical conductivity of the composition at high temperatures, e.g. by the formation of liquid phases that are electrically conductive. This can also result in circuit failure.

The present invention seeks to remedy the problem of mismatch between the thermal expansion coefficients of a substrate it is desired to protect against fire and the ceramic material which confers that protection. In accordance with the present invention it has been found that this problem may be addressed by providing between the substrate and ceramic-forming composition a specific type of interlayer to prevent adhesion of the ceramic to the substrate. Furthermore, the incorporation of a sacrificial layer into the cable design can offer increased protection against circuit failure at elevated temperatures by increasing the insulation resistance in cable applications.

Accordingly, the present invention provides a fire resistant article comprising:

a substrate;

a sacrificial layer provided on the substrate, this layer being formed of a composition comprising an organic polymer and an inorganic filler; and

a ceramic forming layer provided on the sacrificial layer, the ceramic forming layer being formed of a composition which forms a ceramic when exposed to an elevated temperature, wherein the sacrificial layer decomposes at or below the elevated temperature resulting in formation of a layer of the inorganic filler between the substrate and the ceramic such that bonding of the ceramic to the substrate is minimised or prevented.

Use of the sacrificial layer in this way ensures that the substrate and formed ceramic remain separated from each other by a layer which minimises or avoids adhesion of the ceramic to the substrate. The fact that the inorganic filler is non-adherent (to either substrate or ceramic) results in reduced tendency of the ceramic to crack and dislodge during cooling, for example, during exposure to a water spray or jet, because of the differences in the coefficients of thermal expansion between the substrate and the ceramic.

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The inorganic filler remaining after decomposition of the sacrificial layer allows the substrate and formed ceramic to expand and contract independently. In electrical cable applications one consequence of reduced crack formation in the ceramic is that there are reduced pathways for ingress of water and therefore enhanced resistance to circuit failure

5   by electrical shorting on exposure to water. In this case the inorganic filler used preferably has high electrical resistance, thereby further assisting circuit integrity. In all cases the residual filler beneficially provides a barrier to heat transfer, i.e. the residual filler is thermally insulating.

10 The sacrificial layer is typically formed of a composition comprising an organic polymer and an inorganic filler. Herein the term "organic polymer" embraces a variety of polymers which satisfy the following criteria. Firstly, the organic polymer must be one which may be decomposed at a temperature typically encountered in a fire situation to leave little or no solid residue. The organic polymer decomposes at or below the temperature at which

15 the ceramic is formed. Secondly, the organic polymer must be capable of being loaded with suitably high levels of the inorganic filler whilst retaining good processability. The processability of the composition of the sacrificial layer is important, particularly if the composition is to be extruded as is the case in cable applications. It is important that the organic polymer can accommodate sufficiently high levels of inorganic additive such that a

20 substantially continuous layer of inorganic filler remains on the substrate surface after thermal decomposition of the sacrificial layer. The inorganic filler is required to separate the substrate and formed ceramic as described above and, if insufficient inorganic additive is present in the organic polymer, the additive may not fulfil its intended role of preventing direct contact between the substrate and the formed ceramic. The same problem can arise

25 if the inorganic filler is not dispersed homogeneously in the organic polymer. Some degree of contact between the substrate and ceramic may be tolerated in certain applications more so than in others. Electrical cable applications require a continuous layer of inorganic filler between the conductor and ceramic.

30 Desirably, the organic polymer leaves little or no residue on thermal decomposition. It is also important that the polymer be unreactive towards the inorganic filler at elevated

- 5 -

temperature as this may yield reaction products which adhere to the substrate and/or ceramic. Suitable organic polymers are commercially available or may be made by the application or adaptation of know techniques. Examples of suitable organic polymers that may be used are given below.

5

Typically, the composition for the sacrificial layer comprises at least 50% by weight, preferably at least 65% by weight, more preferably at least 75% by weight, inorganic filler.

Useful thermoplastic polymers may be selected from homopolymers of olefins as well as
10 copolymers of one or more olefins. Specific examples of suitable polymers include homopolymers of ethylene, propylene, butene-1, isobutylene, hexene, 1,4-methylpentene-1, pentene-1, octene-1, nonene-1 and decene-1. These polyolefins can be prepared using peroxide, Ziegler-Natta or metallocene catalysts, as is well known in the art. Copolymers of two or more of these olefins may also be employed. The olefins may also be
15 copolymerised with other monomer species such as vinyl or diene compounds. Specific examples of copolymers which may be used include ethylene-based copolymers, such as ethylene-propylene copolymers (for example EPDM), ethylene-butene-1 copolymers, ethylene-hexene-1 copolymers, ethylene-octene-1 copolymers, ethylene-butene-1 copolymers and copolymers of ethylene with two or more of the above mentioned olefins.
20

The thermoplastic polyolefin may also be a blend of two or more of the above mentioned homopolymers or copolymers. For example, the blend can be a uniform mixture of one of the above systems with one or more of polypropylene, high pressure low density polyethylene, high density polyethylene, polybutene-1 and polar monomer-containing
25 olefin copolymers such as ethylene/acrylic acid copolymers, ethylene/methyl acrylate copolymers, ethylene/ethyl acrylate copolymers, ethylene/butyl acrylate copolymers, ethylene/vinyl acetate copolymers, ethylene/acrylic acid/ethyl acrylate terpolymers and ethylene/acrylic acid/vinyl acetate terpolymers.

30 The organic polymer may include styrene monomers, such as polystyrene, SBR, SIS, SBS, SEBS.

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The organic polymer may also be selected from poly(meth)acrylates, polyamides (including nylons), polyesters (such as PET), PVC, ABS, NBR, polyurethanes, epoxides, polycarbonates and polyoxymethylene acetals.

5

As noted, the organic polymer chosen will in part depend upon the intended use of the composition. For instance, in certain applications a degree of flexibility is required of the composition (such as in electrical cable coatings) and the organic polymer will need to be chosen accordingly based on its properties when loaded with the inorganic filler.

10 Polyethylenes and ethylene propylene elastomers have been found to be particularly useful for compositions for cable coatings. Also in selecting the organic polymer account should be taken of any noxious or toxic gases which may be produced on decomposition of the polymer. The generation of such gases may be more tolerable in certain applications than others.

15

After decomposition of the organic polymer a coating of the inorganic filler will remain on the substrate. As noted, for certain applications (e.g. electrical cables) it is desirable that this coating is continuous and mechanically weak. The function of the inorganic additive is to minimise or prevent adhesion between the substrate and ceramic formed at elevated

20 temperature. With this in mind it is important that the inorganic filler is unreactive (with itself, the substrate and the ceramic-forming composition) at the temperatures likely to be encountered in a fire situation. Any reactions involving the inorganic filler may lead to the formation of products which impair the intended role of the inorganic filler.

25 The inorganic filler used in the present invention may be any inorganic material which may be homogenously dispersed in the organic polymer and which will be inert at the temperatures likely to be encountered in a fire situation. The use of the inorganic filler is central to the present invention. Use of an organic polymer alone as the sacrificial layer will not avoid adhesion between the substrate and formed ceramic. In this case the

30 polymer would simply decompose leaving little or no residue. The ceramic would then be in direct contact with the substrate resulting in the problems described above.

Desirably, the inorganic filler has a high melting temperature, for example in excess of 1000°C and, preferably, in excess of 1500°C. The cost of the additive is also likely to be a factor. Examples of suitable inorganic additives include metal oxides, metal hydroxides,

5   talc and clays. Specifically, as well as talc and clays which may be used, mention may be made of alumina, aluminium hydroxide, calcium silicate and zirconia. Combinations of two or more inorganic fillers may be used provided that the combination is inert at the kind of temperatures likely to be encountered in a fire situation.

10 Preferably, the inorganic filler is used in powder form. Equiaxed particles will give the best packing and the thus have the capacity to form the best continuous residual layer after decomposition of the organic polymer. It is possible to use fibrous inorganic additives but this will lead to reduced packing efficiency.

15 The sacrificial layer may include one or more additional functional components provided that these do not interfere with the intended role of the inorganic filler. Such additional components include flame retardant materials and materials that reduce thermal and/or electrical conductivity.

20 The composition used for the sacrificial layer may be prepared by simple blending of the individual components. Any conventional compounding apparatus may be used. If the composition has relatively low viscosity, it may be processed using dispersing equipment, for instance of the type used in the paint industry. Materials useful for cable applications are of higher viscosity (higher molecular weight) and may be processed using a two roll

25 mill, internal mixers, twin-screw extruders and the like. If the organic polymer is to be crosslinked, some heating of the polymer will be required in the presence of a suitable crosslinking agent. Conventional crosslinking agents may be used.

The composition capable of forming a ceramic on heating may be selected from any

30 conventional such compositions. The ceramic forming composition may be silicone polymer-based or include a base composition comprising a blend of silicone and non-

silicone polymers. The compositions may include a variety of inorganic components capable of yielding a ceramic by reaction at elevated temperature. The compositions may also contain additional functional additives such as flame retardants etc. The compositions may be prepared by blending of the individual components using conventional equipment.

5

The substrate may in principle be any material it is desired to protect against fire and upon which it is desired to retain a layer of ceramic material. It will be appreciated that the invention is particularly well suited to application to substrates which have a coefficient of thermal expansion which is quite different from that of the ceramic. Typically, the
10   substrate will be metallic.

Specific examples of practical situations where this invention may be applied include but are not limited to firewall linings and for ferries, trains and other vehicles, fire partitions, screens, ceilings and linings, structural fire protection [to insulate the structural metal
15 . frame of a building to allow it to maintain its required load bearing strength (or limit the core temperature) for a fixed period of time].

This said, the present invention is especially useful for the coating of conductors, i.e. in electrical cable applications. The invention is therefore suitable for the manufacture of
20   electrical cables that can provide circuit integrity in the case of fire. In the design of such cables the composition for the sacrificial layer and ceramic-forming composition can be extruded directly over conductors. This extrusion may be carried out in a conventional manner using conventional equipment. The thickness of the sacrificial layer will usually be from 0.2 to 2 mm, for example from 0.4 to 1.5 mm. The thickness of the ceramic
25   forming layer will depend upon the requirements of the particular standard for the size of conductor and operating voltage. Typically the insulation with have a thickness from 0.6 to 3 mm. For example, for a 35 mm^2 conductor rated at 0.6/1kV to Australian Standards would require an insulation thickness of approximately 1.2 mm. In non-cable applications the appropriate thicknesses of the sacrificial and ceramic forming layers may be
30   determined by experimental testing.

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The present invention also provides use of a sacrificial layer as described herein to minimise or preventing bonding between a substrate and a ceramic forming composition, also as described herein.

5   The following non-limiting example illustrates the present invention.

Example 1

Three 200 mm sections of 35 mm^2 copper conductor were used to make different cable
10   design prototypes. The extrudable compositions examined as sacrificial layers were Composition A (an ethylene propylene rubber heavily filled with predominantly aluminium hydroxide, and containing peroxide) and Composition B (a silicone polymer containing peroxide for thermally induced crosslinking). Composition C (silicone polymer/mica/glass fibre/peroxide 73:20:5:2), which forms a ceramic material when
15   heated at elevated temperatures, was the outer layer in all three prototypes. The prototypes were prepared by simultaneously moulding and curing the composition(s) onto the cable sections. The designs and the layer thicknesses are shown in Table 1.

Table 1

Prototype	Sacrificial Layer Composition (Thickness, mm)	Outer Layer (Ceramic forming layer) Composition (Thickness,mm)
1	Nil	C (1)
2A	A (1)	C (1)
2B	B (1)	C (1)

20

All three prototype cables were then heated in a furnace to 1000°C in air for 30 minutes. They were then removed from the furnace and allowed to cool to room temperature, their behaviour during cooling being monitored.

Prototype cable 1, which had no layer between the conductor and the ceramic forming compositions, showed no visible cracking of the ceramic layer when it was removed from the furnace. However, during cooling the ceramic insulation gradually cracked and sections spalled off the cable.

5

Prototype cable 2A (in accordance with the present invention), showed no visible cracking of the ceramic layer when it was removed from the furnace and even after 15 minutes of cooling no cracking or loss of insulation occurred.

10 Prototype cable 2B, with the silicone polymer interlayer, had with some circumferential cracking when it was removed from the furnace, and after 8 minutes cooling significant cracking had occurred and a large section of insulation from the middle of the cable spalled off the conductor.

15 Visual and microscopical examination of the cables after the test showed that the ceramic layer in prototype 1 had bonded strongly to the oxide layer on the copper conductor. Thermal expansion mismatch between the conductor and the ceramic resulted in the disintegration of the ceramic layer during cooling with dislodged ceramic pieces attached to a thin layer of copper oxide that had become delaminated from the conductor surface.

20 For prototype 2A a continuous powdery residue in between the conductor and the outer ceramic layer was observed. This residue appeared to have not reacted with or bonded to either the conductor or the ceramified insulation. Thus, it effectively prevented any bond from forming between the conductor and the insulation. Contrasting this, the interlayer in prototype 2B appeared hard and glassy and had bonded to the conductor and the ceramic

25 layer.

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Polymers Australia Pty Ltd

Freehills Carter Smith Beadle

30 Patent attorneys for the applicant.